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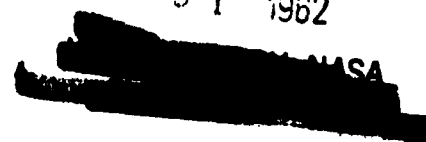
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Interaction Energies from Scattering Cross Sections of
Hydrogen Ions in CH_4 , CF_4 , C_2H_6 , and C_2F_6 .*

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ABSTRACT

The potential energy curves for the interactions between hydrogen ions (H^+ , H_2^+) and CH_4 , C_2H_6 , CF_4 , and C_2F_6 have been determined from the elastic scattering cross section measurements of Simons and coworkers. The scattering measurements indicate no minimum in the H^+-CH_4 potential curve as one might expect from the fact that mass spectrographic results indicate a proton affinity of 5 ev for CH_4 . Reasons are suggested why no minimum is indicated.

Various crude semi-empirical schemes are suggested for correlating the potential curves for the different interaction systems. All suggested schemes are tested on the experimental results and are found to reproduce the measured potentials to within a factor of two.

* This research has been supported in part by the National Aeronautics and Space Administration.

INTRODUCTION

The present paper reports on the results of some calculations of short-range forces between hydrogen ions (H^+ , H_2^+) and polyatomic molecules. The elastic scattering measurements of hydrogen ions in CH_4 ,¹ C_2H_6 ,² CF_4 , and C_2F_6 ³ have been used to determine the parameters in assumed force laws. The potential functions so obtained have then been used as a basis in judging various semi-empirical schemes to obtain forces between ions and complicated polyatomic molecules.

Potential curve information can, of course, be obtained from the ab initio calculations of molecular quantum mechanics. Unfortunately, this approach is still too complicated to be practicable for any but the simplest systems. One such study was made of the ground state of protonated methane, CH_5^+ , by Yamazaki⁴ according to a revised Heitler-London-Slater-Pauling method. The extension, however, of a study like this to even slightly more complicated systems involves assumptions that severely qualify the results. Less accurate studies have also been made, such as the simple UAS-MO calculations on CH_5^+ by Higuchi.⁵ Here the discrepancy between the calculated proton affinity and the experimentally observed value seems unavoidable in light of the roughly approximated MO's. In lieu of necessary refinements in such studies, indirect and semi-empirical methods are often necessary and desirable.

In the present study, various semi-empirical schemes to correlate the experimental potential curves for the various interacting species were tried. The most sophisticated scheme used was to assume that the ion-molecule potential was due simply to the sum of the potentials between the ion and the peripheral atoms of the molecule. This follows a suggestion made earlier by Amur and coworkers⁶ in their treatment of the interactions of He with CH_4 and CF_4 . With this assumption it has been possible to predict for example the $H^+-C_2H_6$ potential curve from a knowledge of the H^+-CH_4 potential curve. The same scheme was used to predict with surprising accuracy the $H^+-C_2F_6$, $H_2^+-C_2H_6$, and $H_2^+-C_2F_6$ potentials from the H^+-CF_4 , $H_2^+-CH_4$ and $H_2^+-CF_4$

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potentials, respectively.

The second general scheme used was to assume that C_2H_6 and C_2F_6 behaved like diatomic molecules and that the ion-molecule potential was just the sum of interactions between the ion and two point centers of forces which were taken to be CH_4 or CF_4 molecules, respectively. This approach also gave surprisingly good agreement with the experimental curves.

The third and crudest scheme was to assume not only that C_2H_6 and C_2F_6 behaved like diatomic molecules but also that the H_2^+ acted as a single point center of force. In this way, the $H_2^+-C_2H_6$ and $H_2^+-C_2F_6$ potentials were calculated from the $H_2^+-CH_4$ and $H_2^+-CF_4$ potentials, respectively, with results comparable to the previous two approaches.

POTENTIALS FROM ELASTIC SCATTERING CROSS SECTIONS

Simons and coworkers¹⁻³ analysed their scattering measurements for the systems of interest under the assumption that the potentials were monotonic attractive inverse power ones. Such an assumption appears quite unreasonable⁷ at internuclear distances of 1.5 to 3.0A, the range of distance covered by their experiments:

Plots of $\bar{S}^{1/2}$ vs $\log W$, where \bar{S} is the measured elastic cross section and W is the beam energy, were linear within experimental error for each of the reacting systems studied. This suggested that a simple exponential potential function (assumed to be repulsive) would explain the scattering measurements over the range of energy studied.⁷ Hence, the usual procedure⁷ was followed in evaluating the parameters, V_0 and a in the potential expression

$$V(r) = V_0 e^{-ar} \quad (1)$$

for each of the systems under consideration. The potential functions obtained and their range of validity are tabulated in Table I.

THE H^+ - CH_4 POTENTIAL

Some remarks should be made about the H^+ - CH_4 potential determined from these scattering measurements. As mentioned above, the experimental results indicated that the potential was of an exponential form which we have assumed to be repulsive.

On the other hand, mass spectrographic measurements⁸ indicate that CH_5^+ is a stable species with a binding energy of more than 5 ev. Yamazaki's theoretical calculations⁴ are in substantial agreement with this estimate. However, it does not seem possible to explain the scattering measurements for the H^+ - CH_4 system on the basis of a bound state with a proton affinity of 5 ev. The curve of $\log \bar{S}$ vs $\log W$ does not show the curvature one would expect from scattering due to a potential curve with such a deep minimum.⁷ Indeed our attempts to fit the scattering results with a Morse function model led to physically ridiculous parameters. One possible explanation would be that the CH_4 molecule does not have time to rearrange itself from a tetrahedron towards the trigonal bipyramid structure of CH_5^+ as the fast moving H^+ approaches, so that the normal CH_5^+ curve is not followed.

Also, the H^+ sees all possible orientations of the CH_4 molecules as it approaches and it is likely that only relatively few directions of approach would follow the normal CH_5^+ bound curve. For purposes of explaining the present experiments it appears as if the CH_4 is "frozen" in its normal configuration during the scattering.

C_2H_6 and C_2F_6 Potentials from Effective

H^+ -H and H^+ -F Potentials

We now wish to generate potential expressions for the interactions of hydrogen ions (H^+ , H_2^+) with C_2H_6 and C_2F_6 from a previous knowledge of the interactions of hydrogen ions with C_2H_6 and C_2F_6 . The first approximation one could make is to assume, for example, that the H^+ - CH_4 and H^+ - C_2H_6 potentials were due solely to the sum of the interactions between the H^+ and the peripheral hydrogen atoms on the carbons. With this assumption it is possible to

obtain an effective $H^+ \cdots H$ potential from the experimental $H^+ - CH_4$ potential and use this to determine the $H^+ - C_2H_6$ potential.

This can be done in the following way. Previously, it has been shown¹⁰ that if the potential energy between two atoms, A and B, is of the form $V = V_0 e^{-aR}$, and if one of the atoms is at a distance $d/2$ from the center of mass (see Fig. 1), then the potential averaged over all orientations of the B atom, always keeping the distance $d/2$ fixed, is given by

$$\langle V(R) \rangle = V_0 e^{-aR} (a^2 R d)^{-1} \left[2(aR+1) \sinh(ad/2) - 2\left(\frac{ad}{2}\right) \cosh(ad/2) \right], \quad (2)$$

where R is the distance from the center of mass to the A atom. With our assumptions, the measured $H^+ - CH_4$ potential should be just four times Eq. (2) if $d/2$ is taken to be the C-H distance in CH_4 and V_0 and a are the parameters in the effective potential between the H^+ and a hydrogen atom in methane. V_0 and a were determined by successive approximations until four times Eq. (2) fitted the $H^+ - CH_4$ potential within experimental error. The $H^+ - C_2H_6$ potential could then be determined from these parameters. Under our assumptions, this potential should be six times Eq. (2) with $d/2$ being the distance from a peripheral H atom and the midpoint of the C-C bond in ethane. The result is given in Table II A and is shown along with the experimentally determined $H^+ - C_2H_6$ potential in Fig. 2. The two curves agree to within a factor of two over the ranges covered in the experiments.

An exactly similar procedure was followed for the $H^+ - CF_4$ and $H^+ - C_2F_6$ potentials and the result is also given in Table II A. The $H^+ - C_2F_6$ curve along with the experimental one is shown in Fig. 3. They agree to within a factor of two.

The $H_2^+ - CH_4$ and $H_2^+ - C_2H_6$ potentials can be handled in a somewhat similar manner if one assumes that the potential is just the sum of the potentials between the hydrogen in H_2^+ and the peripheral atoms in CH_4 and C_2H_6 . Instead of Eq.(2), we have¹¹ (see Fig. 1b)

$$\langle V(R) \rangle = V_0 e^{-aR} (a^3 R d_1 d_2)^{-1} \left[4(aR+2) \sinh(ad_1/2) \sinh(ad_2/2) - 4(ad_1/2) \sinh(ad_2/2) \cosh(ad_1/2) - 4(ad_2/2) \sinh(ad_1/2) \cosh(ad_2/2) \right]. \quad (3)$$

This corresponds to a potential between two species A and B which are at fixed distances, $d_1/2$ and $d_2/2$, from two points O and O', the potential being averaged over all relative orientations of A and B subject only to $d_1/2$ and $d_2/2$ being held fixed. V_0 and a are again the parameters in the potential between A and B, R is the distance between O and O'. If our assumptions are correct, the $H_2^+-CH_4$ potential should be eight times Eq. (3) if d_1 is the bond distance in H_2^+ and $d_2/2$ is the bond length in methane. V_0 and a were accordingly determined by successive approximations until the $H_2^+-CH_4$ curve was reproduced to within experimental error. With these parameters, the $H_2^+-C_2H_6$ potential was easily determined since it should be just twelve times Eq. (3) if $d_2/2$ is the distance from a peripheral hydrogen atom and the midpoint of the C-C bond in ethane. The result is given in Table IIA and the calculated curve along with the experimental curve is shown in Fig. 4. Again the curves agree to within a factor of two.

The same procedure was used to correlate the $H_2^+-CF_4$ and $H_2^+-C_2F_6$ ¹² potentials with the results given in Table IIA. The experimental and calculated curves are shown in Fig. 5. The agreement is within a factor of two.

POTENTIALS FROM POINT CENTER OF FORCE ASSUMPTIONS

It is interesting to compare the above approximate procedure with one which assumes that the interactions are between various point centers of force on the interacting systems. For example, ethane was regarded as two methane molecules separated by the normal C-C distance in ethane. Then from Eqs. (2) and (3) one can easily calculate the $H^+-C_2H_6$, $H^+-C_2F_6$, $H_2^+-C_2H_6$, and $H_2^+-C_2F_6$ potentials. In these cases the parameters V_0 and a are simply those obtained from the experimental scattering data on the corresponding H^+-CH_4 , H^+-CF_4 , $H_2^+-CH_4$, and $H_2^+-CF_4$ systems. The results are given in Table IIB and are shown in Figs. 2-5. A comparison of these values with the results

of the former approximation shows that the average calculated potential increased by from ten to thirty percent for all systems. This means that the experimental potentials were more closely reproduced in all but the $\text{H}^+-\text{C}_2\text{H}_6$ system by a crude assumption involving point centers of force. These two approximate methods of deducing average ion-molecule potentials lead to strikingly similar results, particularly for the $\text{H}_2^+-\text{C}_2\text{H}_6$ interaction.

A further calculation on the $\text{H}_2^+-\text{C}_2\text{H}_6$ and $\text{H}_2^+-\text{C}_2\text{F}_6$ systems assumed that H_2^+ was one point center of force. These potentials were then calculated from Eq.(2) with V_0 and a determined from the corresponding experimental H_2^+-CH_4 and H_2^+-CF_4 potentials. This assumption, within experimental error, did not appreciably change the results of the other point center of force assumption. The results of this calculation are given in Table IIC and are shown in Figs.(4) and (5).

SUMMARY

The potentials for the interactions between hydrogen ions (H^+, H_2^+) and CH_4 , C_2H_6 , CF_4 , and C_2F_6 have been determined at small distances of interaction from the experimental elastic scattering cross sections for the various systems. The H^+-CH_4 potential governing the scattering appears to be purely repulsive. There is no indication that this potential has a deep minimum as one might expect from the existence of the stable CH_5^+ ion and the mass spectrographic estimate of a proton affinity of more than 5 ev for CH_4 . It is postulated that the CH_4 molecule in these scattering measurements does not have time to rearrange itself as the fast moving H^+ approaches and so the normal potential curve is not followed.

It has been possible to correlate H^+-CH_4 , H_2^+-CH_4 , H^+-CF_4 , and H_2^+-CF_4 potentials with the $\text{H}^+-\text{C}_2\text{H}_6$, $\text{H}_2^+-\text{C}_2\text{H}_6$, $\text{H}^+-\text{C}_2\text{F}_6$ and $\text{H}_2^+-\text{C}_2\text{F}_6$ potentials by several crude semi-empirical approximations. One approximation assumes that the potential between the ion and the organic molecule is due mainly to the sum of the potentials between the peripheral atoms and the ion. This assumption enables one to calculate the $\text{H}^+-\text{C}_2\text{H}_6$ potential to within a factor of two from a previous knowledge of the H^+-CH_4 potential. The same procedure

gives similar results for the other pairs of interacting systems.

The second scheme is a point center of force approximation in which it is assumed that C_2H_6 (C_2F_6) looks to the oncoming ions like two CH_4 (CF_4) molecules separated by the normal C-C bond distance. The potentials so calculated are generally in even better agreement with the measured potentials than the previous approximation. The further assumption that H_2^+ is a single point center of force leads to results almost identical with the second approximation scheme.

These results suggest that it may be possible to predict interactions between complex systems with fair accuracy on the basis of a limited number of measurements on simpler systems.

ACKNOWLEDGMENT

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TABLE I. Average potential functions of hydrogen ion interactions with methane, methforane, ethane and ethforane from scattering data.

System	Potential (ev)	Range (A)
$\text{H}^+ - \text{CH}_4$	$1.04 \times 10^4 \exp(-3.627 R)$	1.97 - 3.39
$\text{H}_2^+ - \text{CH}_4$	$2.74 \times 10^4 \exp(-4.192 R)$	1.94 - 2.94
$\text{H}^+ - \text{C}_2\text{H}_6$	$1.84 \times 10^3 \exp(-2.546 R)$	2.04 - 3.27
$\text{H}_2^+ - \text{C}_2\text{H}_6$	$6.99 \times 10^4 \exp(-3.754 R)$	2.34 - 3.47
$\text{H}^+ - \text{CF}_4$	$4.94 \times 10^1 \exp(-1.333 R)$	1.42 - 3.20
$\text{H}_2^+ - \text{CF}_4$	$1.88 \times 10^2 \exp(-1.941 R)$	1.76 - 3.16
$\text{H}^+ - \text{C}_2\text{F}_6$	$1.81 \times 10^2 \exp(-1.452 R)$	2.02 - 4.45
$\text{H}_2^+ - \text{C}_2\text{F}_6$	$6.16 \times 10^2 \exp(-1.850 R)$	2.53 - 4.16

TABLE II. Average Potential functions of hydrogen ion interactions with ethane and ethforane from hydrogen ion -methane and -methforane scattering data.

System	Potential (ev)	Range (A)
A. From Effective H^+-H, H^+-F Potentials		
$H^+-C_2H_6$	$2.52 \times 10^4 \exp(-3.452 R)$	2.17 - 3.50
$H_2^+-C_2H_6$	$2.45 \times 10^4 \exp(-3.517 R)$	2.16 - 3.07
$H^+-C_2F_6$	$8.64 \times 10^1 \exp(-1.293 R)$... - 3.33
$H_2^+-C_2F_6$	$2.02 \times 10^2 \exp(-1.706 R)$	2.11 - 3.30
B. Assumption: C_2H_6 and C_2F_6 are Di-point Centers of Force		
$H^+-C_2H_6$	$3.92 \times 10^4 \exp(-3.536 R)$	2.07 - 3.45
$H_2^+-C_2H_6$	$1.07 \times 10^5 \exp(-4.003 R)$	2.05 - 3.01
$H^+-C_2F_6$	$9.60 \times 10^1 \exp(-1.297 R)$	1.55 - 3.26
$H_2^+-C_2F_6$	$3.89 \times 10^2 \exp(-1.882 R)$	1.71 - 3.13
C. Assumption: $H_2^+-C_2H_6$ and $H_2^+-C_2F_6$ are Tri-point Centers of Force.		
$H_2^+-C_2H_6$	$1.25 \times 10^5 \exp(-4.059 R)$	2.05 - 3.01
$H_2^+-C_2F_6$	$4.00 \times 10^2 \exp(-1.890 R)$	1.87 - 3.22

FIGURE CAPTIONS

Fig. 1. Diagram illustrating distances involved in obtaining average molecule-molecule potentials from a knowledge of effective atom-atom potentials.

Fig. 2. $\text{H}^+-\text{C}_2\text{H}_6$ potentials obtained by different methods.

Curve (a): from scattering data.

Curve (b): from peripheral atom treatment.

Curve (c): from point center of force assumptions.

Fig. 3. $\text{H}^+-\text{C}_2\text{F}_6$ potentials obtained by different methods.

Curve (a): from scattering data.

Curve (b): from peripheral atom treatment.

Curve (c): from point center of force assumption.

Fig. 4. $\text{H}_2^+-\text{C}_2\text{H}_6$ potentials obtained by different methods.

Curve (a): from scattering data.

Curve (b): from peripheral atom treatment.

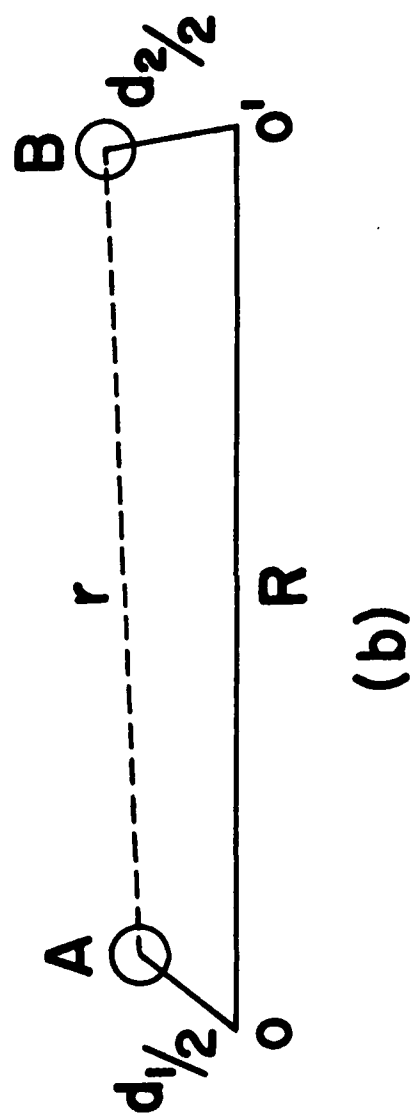
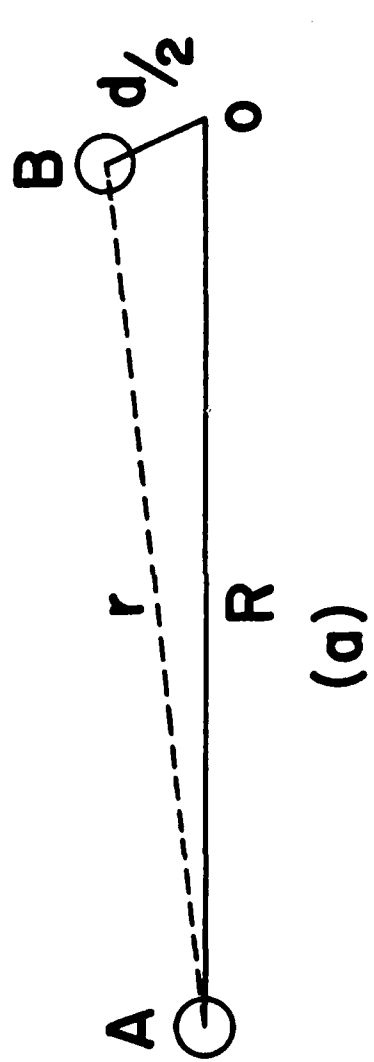
Curve (c): from point center of force assumption.

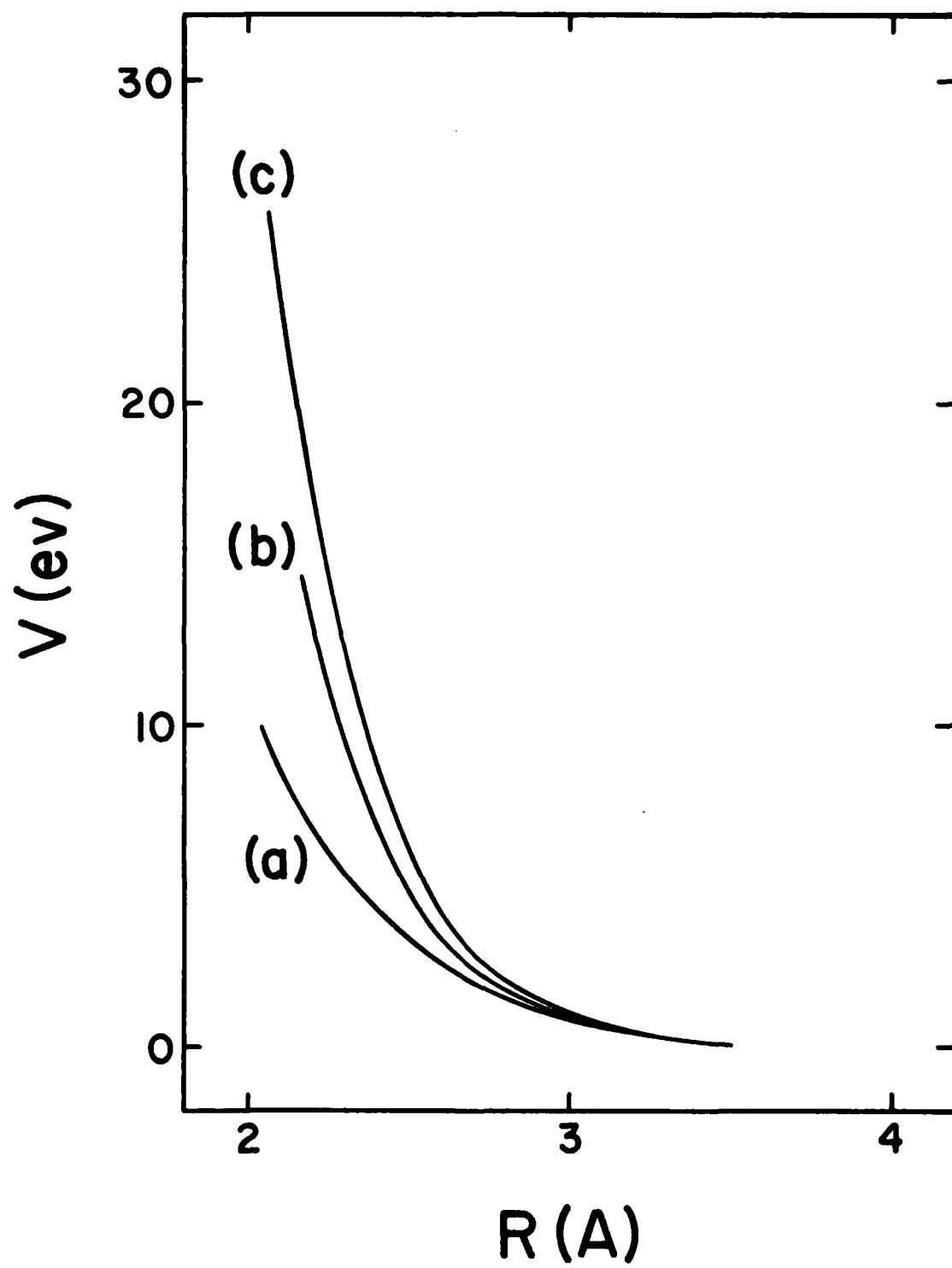
Fig. 5. $\text{H}_2^+-\text{C}_2\text{F}_6$ potentials obtained by different methods

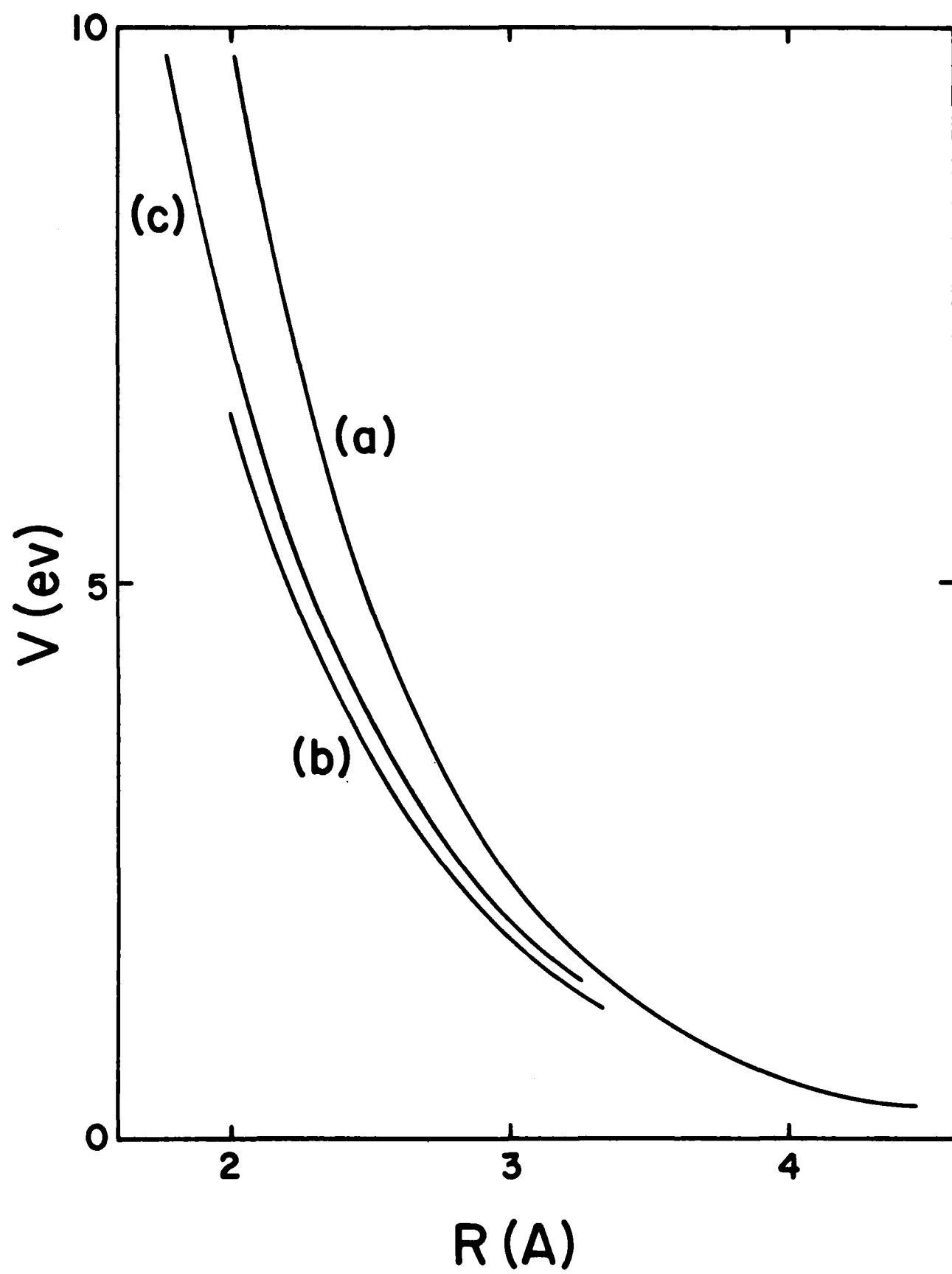
Curve (a): from scattering data.

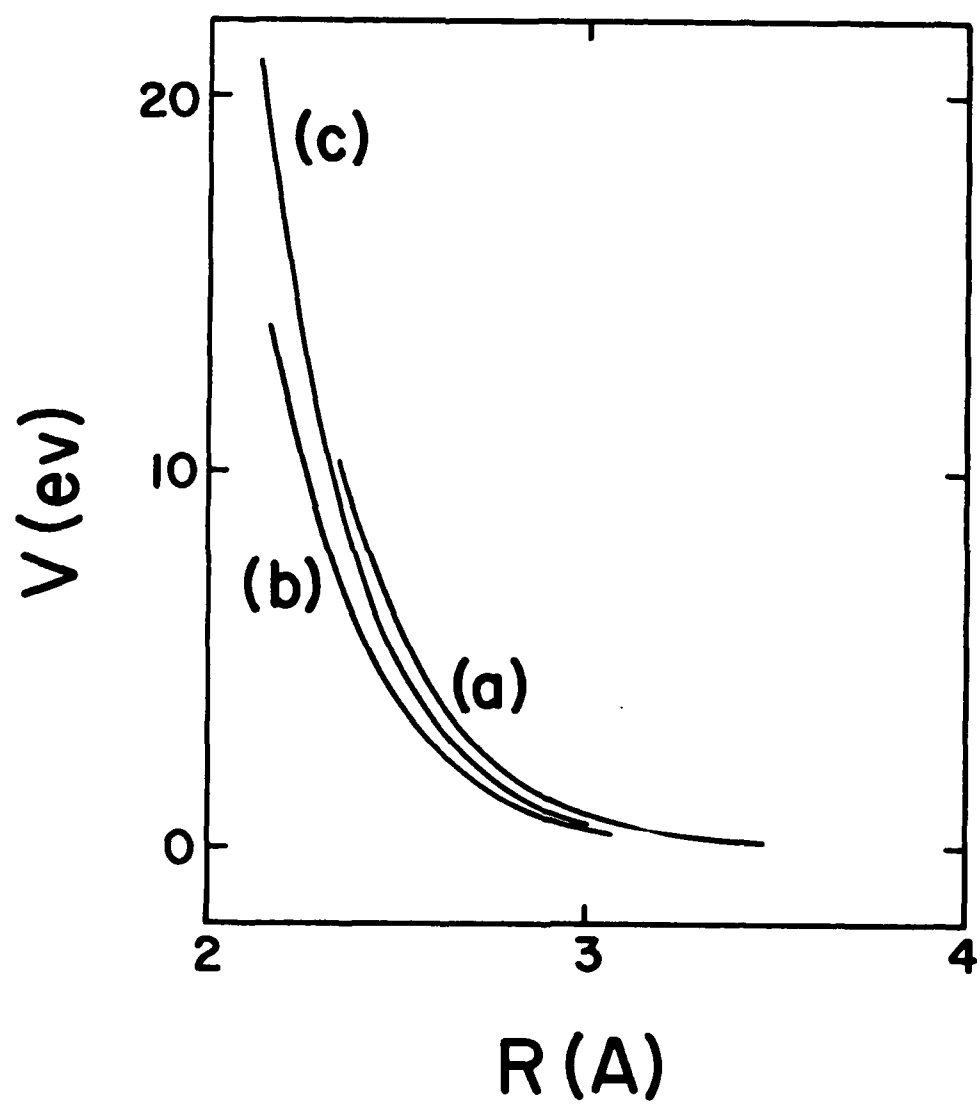
Curve (b): from peripheral atom treatment

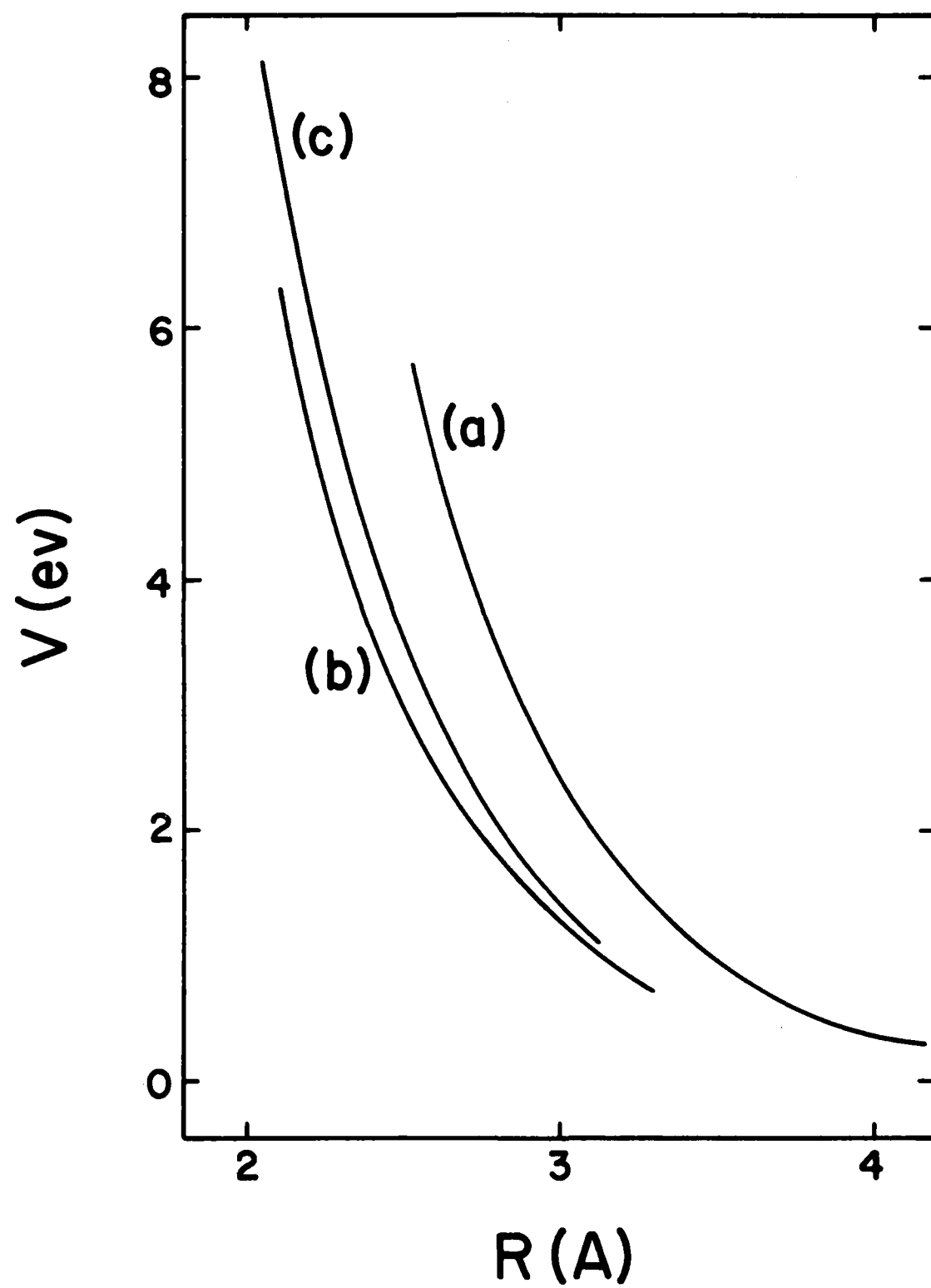
Curve (c): from point center of force assumption.











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